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(54) FLAME RETARDANT ADHESIVE AND FLAME RETARDANT ADHESIVE FILM USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To impart good electric insulating properties, adhesive properties and moreover flame retardancy equal to that of a halogen-based flame retardant to a nonhalogen-based flame retardant adhesive.
SOLUTION: This flame retardant adhesive is composed of (A) a polyester- based resin, (B) a polyphosphoric acid-based flame retardant and (C) a non- polyphosphoric acid-based organic flame retardant containing nitrogen. Besides, the flame retardant adhesive film comprises a flame retardant adhesive layer composed of the flame retardant adhesive formed on a insulating substratal film.

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CLAIMS

[Claim(s)]
[Claim 1] The following components (A), (B), and (C) : (A) Polyester system resin; (B) Polyphosphoric acid system flame retarder; And (C) Fire-resistant adhesives characterized by containing a non-polyphosphoric acid system nitrogen content organic flame retarder.
[Claim 2] Fire-resistant adhesives according to claim 1 which carry out 5-100 weight section content of the polyphosphoric acid system flame retarder of a component (B) to the polyester system resin 100 weight section of a component (A).
[Claim 3] Fire-resistant adhesives according to claim 1 which carry out 10-60 weight section content of the polyphosphoric acid system flame retarder of a component (B) to the polyester system resin 100 weight section of a component (A).
[Claim 4] Fire-resistant adhesives according to claim 1 to 3 whose polyphosphoric acid system flame retarder of a component (B) is a polyphosphoric acid melamine.
[Claim 5] Fire-resistant adhesives according to claim 1 to 4 which carry out 30-150 weight section content of the non-polyphosphoric acid system nitrogen content organic flame retarder of a component (C) to the polyester system resin 100 weight section of a component (A).
[Claim 6] Fire-resistant adhesives according to claim 1 to 4 which carry out 40-100 weight section content of the non-polyphosphoric acid system nitrogen content organic flame retarder of a component (C) to the polyester system resin 100 weight section of a component (A).
[Claim 7] Fire-resistant adhesives according to claim 1 to 6 whose non-polyphosphoric acid system nitrogen content organic flame retarder of a component (C) is a melamine SHIANU rate.
[Claim 8] The fire-resistant adhesive film characterized by forming the fire-resistant glue line which consists of fire-resistant adhesives according to claim 1 to 7 on an insulating base material film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the fire-resistant adhesives of the non halogen system used in case the surface protective layer of various electronic parts, such as a flexible printed circuit board in the case of production of a flat cable, is formed, and the fire-resistant adhesive film using it. It has good electric insulation and a good adhesive property in more detail, and is related with the fire-resistant adhesive film using the non halogen system fire retardancy adhesives and it which have the fire retardancy which is equal to the halogen system fire retardancy adhesives which moreover used the halogen series flame retardant.
[0002]
[Description of the Prior Art] The flat cable of the structure which covered the conductor of the shape of two or more line is known for the adhesive film of two sheets with which the adhesives layer was formed on the base material film. Such a flat cable is widely used for wiring of the AV equipment with which high density assembly of the recent years was carried out, or a computer machine.
[0003] by the way, a flat cable -- receiving -- the conductor from the electric application and a viewpoint of accident prevention -- the electric insulation and fire retardancy with a good component (namely, adhesive film which consists of a base material film and an adhesives layer) of an except are wanted to be shown.
[0004] For this reason, in the adhesives layer of an adhesive film which is used for a flat cable, inorganic fillers, such as a silica, clay, and an antimony compound, etc. were added from the former as halogen series flame retardants (for example, decabromodiphenyl ether, hexa BUROMO diphenyl ether, etc.) or a fire-resistant assistant. However, from the consideration to the latest earth environmental protection, as a flame retarder added in an adhesives layer, it replaces with a halogen series flame retardant, and a non halogen series flame retardant is used. For example, JP,6-338225,A has proposed adding non halogen series flame retardants, such as red phosphorus, phosphoric ester, and a magnesium hydroxide, in the polyester fire retardancy layer of the adhesive tape for flat cables. Moreover, JP,9-221642,A has proposed carrying out flameproofing of the adhesives layer formed the thermoplastic polyester system resin base material which constitutes the adhesive film for flat cables, or on it with a phosphorus series flame retardant.
[0005] Moreover, the fire-resistant adhesive film same as a surface-protection film of various electronic parts, such as a flexible printed circuit board used for precision electronic equipment, as what is used for the flat cable is used.
[0006]
[Problem(s) to be Solved by the Invention] By the way, when using a flat cable as wiring of the various products (for example, the Ayr back and medical equipment of an automobile) in connection with the insurance of the body, in order to secure safety stably, very high electric insulation is required. Moreover, also in order to secure the engine-performance dependability of various precision electronic equipment, high electric insulation is demanded from the surface-protection film of various electronic parts, such as a flexible printed circuit board.
[0007] However, in the case of the adhesive tape indicated by the above-mentioned official report or an adhesive film, there is a problem that the electric resistance of adhesive tape or an adhesive film cannot be made high enough because of the hygroscopicity which the non halogen series flame retardant itself to be used shows, or ionicity.
[0008] Moreover, a non halogen series flame retardant which was mentioned above Compared with the conventional halogen series flame retardant, fire retardancy is not enough in essence, and in order to realize desired electric insulation, it is necessary to raise the content in the adhesives layer of a non halogen series flame retardant. For this reason, the adhesive strength of an adhesives layer declines, and in case it is

production of a flat cable, there is a problem that an adhesives layer and a conductor become easy to exfoliate mutually, and the cohesive force of an adhesives layer declines in the case of the laminating of the surface-protection film to the front face of electronic parts, such as a flexible printed circuit board.
[0009] This invention aims at offering the fire-resistant adhesives of the non halogen system which is going to solve the technical problem of a Prior art, has good electric insulation and a good adhesive property, and has the fire retardancy which is moreover equal to a halogen series flame retardant, and the fire-resistant adhesive film using it.
[0010]
[Means for Solving the Problem] As base resin for fire-resistant adhesives, this invention persons use polyester system resin with comparatively low hygroscopicity, and came to complete a header and this invention for the ability of the above-mentioned object to be attained by using together non-polyphosphoric acid system nitrogen content organic flame retarders, such as polyphosphoric acid system flame retarders, such as a polyphosphoric acid melamine, and a melamine SHIANU rate, as a flame retarder.
[0011] That is, this invention is the following components (A), (B), and (C): (A). Polyester system resin; (B) Polyphosphoric acid system flame retarder; And (C) The fire-resistant adhesives characterized by containing a non-polyphosphoric acid system nitrogen content organic flame retarder are offered.
[0012] Moreover, this invention offers the fire-resistant adhesive film characterized by preparing the fire-resistant glue line which consists of these fire-resistant adhesives on an insulating base material film.
[0013]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.
[0014] The fire-resistant adhesives of this invention contain (Component A) polyester system resin, (Component B) polyphosphoric acid system flame retarder, and a (Component C) non-polyphosphoric acid system nitrogen content organic flame retarder as an indispensable component.
[0015] In the fire-resistant adhesives of this invention, the polyester system resin of a component (A) functions as a membrane formation component as an adhesive resinous principle. The reason for having chosen polyester system resin has comparatively low hygroscopicity compared with the polyamide resin generally used as an adhesion component, and is because film reinforcement is satisfactory practically and moreover excellent also in electric insulation.
[0016] as such polyester system resin -- an acid component (for example, a terephthalic acid --) Isophthalic acid, diphenyl dicarboxylic acid, an adipic acid, a sebacic acid, the multiple-valued carboxylic acid that has phosphoric acid residue in a molecule, a guru phthalic acid, trimellitic acid, sulfoisophtharate sodium, etc., a dialcohol component (for example, ethylene glycol and 1,4-butanediol --) The polyester system resin formed from 1, 4-JISHIKURO hexane dimethanol, 1, 4-cyclohexane dimethylol, a diethylene glycol, the ethyleneoxide addition TORIMECHI roll propanol of bisphenol A, etc. can be mentioned. Especially, the phosphorus internal polyester system resin (refer to claim 1 of JP,8-60108,A, a paragraph 0010, a paragraph 0011, and paragraph 0015 grade) which has phosphoric acid residue in a molecule is desirable in respect of high fire retardancy.
[0017] from a viewpoint of securing sufficient membrane formation nature even if the number average molecular weight of the polyester system resin of a component (A) is the case where the polyphosphoric acid system flame retarder of the component (B) which fire-resistant adhesives mention later, and the non-polyphosphoric acid system nitrogen content organic flame retarder of a component (C) are contained so much -- desirable -- 3000-100000 -- it is the range of 10000-50000 more preferably.
[0018] Moreover, when fire-resistant adhesives are applied to production of a flat cable, the glass transition point of the polyester system resin of a component (A) is 0-70 degrees C more preferably -40-100 degrees C so that heat adhesion can be carried out good to a line-like conductor.
[0019] The polyphosphoric acid system flame retarder of a component (B) is a non halogen series flame retardant, and even if it uses it independently, it shows the high fire retardancy which is equal to the conventional halogen series flame retardant. However, since there is an inclination which lowers the electric resistance of the fire-resistant whole adhesives, it is unsuitable for an electronic equipment application, and is used together with the non-polyphosphoric acid system nitrogen content organic flame retarder of the component (C) mentioned later.
[0020] Specifically as a polyphosphoric acid system flame retarder of a component (B), there are a polyphosphoric acid melamine, polyphosphoric acid ammonium, etc. The point that the inclination which lowers electric resistance especially is small to a polyphosphoric acid melamine is desirable.
[0021] since the electric resistance of the whole adhesives will be reduced if many [if there is too little amount of the polyphosphoric acid system flame retarder used of this component (B), sufficient fire-

resistant effectiveness will not be acquired, and / too] -- the polyester system resin 100 weight section of a component (A) -- receiving -- desirable -- the 5 - 100 weight section -- more -- desirable -- 10 - 60 weight section -- it is 10 - 40 weight section still more preferably.
[0022] While the non-polyphosphoric acid system nitrogen content organic flame retarder of a component (C) is a non halogen series flame retardant which does not contain polyphosphoric acid residue, when fire-resistant adhesives are made to contain it, it is a flame retarder to which electric resistance is not reduced. As a non-polyphosphoric acid system nitrogen content organic flame retarder of such a component (C), melamine derivatives, such as a melamine (cyanurtriamide), AMUMERIN (cyanuric acid diamide), AMUMERIDO (cyanuric acid monoamide), MERAMU (it presumes in case of [3 and 5-(NH2) C3N3] NH), a melamine SHIANU rate (condensation of a melamine and cyanuric acid), melamine resin, gay guanamine, benzoguanamine, and acetoguanamine, etc. can be mentioned preferably. Also in these, a melamine, a melamine SHIANU rate, or benzoguanamine is desirable from points, such as dispersibility to polyester system resin, miscibility, and an adhesive property, and especially a melamine SHIANU rate is desirable especially.
[0023] since too much amount of the non-polyphosphoric acid system nitrogen content organic flame retarder used of a component (C) will become inadequate [bond strength] if sufficient fire-resistant effectiveness will not be acquired if too few, but there is -- the polyester system resin 100 weight section of a component (A) -- receiving -- desirable -- the 30 - 150 weight section -- it is the 40 - 100 weight section more preferably.
[0024] In the fire-resistant adhesives of this invention, the flame retarder of an inorganic system and the so-called fire-resistant assistant can be added as a component (D) by within the limits at the object of this invention. As an example of a fire-resistant assistant, a calcium carbonate, a magnesium oxide, a magnesium hydroxide, an aluminum hydroxide, etc. can be mentioned.
[0025] since an adhesive property will fall if many [if there are too few fire-resistant assistants of a component (D), the addition effectiveness will not fully be acquired, and / too] -- the polyester system resin 100 weight section of a component (A) -- receiving -- desirable -- the 5 - 150 weight section -- it is the 10 - 100 weight section more preferably.
[0024] In the fire-resistant adhesives of this invention, it is the range which does not spoil the effectiveness of this invention, and further various additives, for example, an organic solvent, an antioxidant, a metallic corrosion inhibitor, a coloring agent (a pigment, color), the various coupling agents that raise the cohesive force between adhesion component resin and a flame retarder, a cross linking agent, a bridge formation assistant, a bulking agent, an antistatic agent, and a fire-resistant catalyst may be added suitably.
[0025] The fire-resistant adhesives of this invention can manufacture other addition components by mixing to homogeneity a component (A), a component (B), a component (C), and if needed.
[0026] The fire-resistant adhesives of this invention can be used with gestalten, such as a solution, a paste, and a pellet.
[0027] Next, the fire-resistant adhesive film of this invention is explained.
[0028] The fire-resistant adhesive film of this invention has the structure where the fire-resistant glue line which consists of above-mentioned fire-resistant adhesives was prepared on the insulating base material film. Therefore, this fire-resistant adhesive film turns into a fire-resistant adhesive film which can realize fire retardancy which is equal to a halogen series flame retardant, maintaining good electric insulation and a good adhesive property.
[0029] Although the thickness of a fire-resistant glue line changes with purposes of using a fire-resistant adhesive film etc., it is usually 10-100 micrometers.
[0030] As an insulating base material film, a polyethylene terephthalate film, a polyethylenenaphthalate film, a polyimide film, a polyphenylene sulfide film, a poly propylene oxide film, a polyethylene film, a polypropylene film, a polyamide film, etc. can be mentioned. Moreover, the thickness can respond in activity eye, and can be chosen suitably, for example, can be set to several micrometers - hundreds of micrometers.
[0031] The fire-resistant adhesive film of this invention can be manufactured carrying out spreading desiccation of the organic solvent (for example, toluene) content solution of the fire-resistant adhesives of this invention mentioned above on insulating base material films, such as polyethylene terephthalate, and forming a fire-resistant glue line, or by carrying out melting extrusion membrane formation of the fire-resistant adhesives on an insulating base material film.
[0032] Although it can use as a surface-protection film of various electronic parts, such as a flexible printed circuit board and a rigid printed circuit board, the fire-resistant adhesive film of this invention can be

preferably used, in case especially a flat cable is produced. For example, a flat cable is producible by carrying out the laminating of the fire-resistant adhesive film from the upper and lower sides of a conductor, after arranging two or more conductors to parallel. Here, a fire-resistant adhesive film is producible by the heat laminating method which uses the roll heated in the range of 80-200 degrees C by existence of a flame retarder on the occasion of a laminating since ordinary temperature was not enough as adhesive strength.
[0033]
[Example] Hereafter, an example explains this invention concretely.
[0034] With the loadings shown in one to examples 1-7 and example of comparison 3 (preparation of fire-resistant adhesives) table 1, or a table 2, polyester system resin (ERITERU series (saturated polyester resin), Unitika, Ltd. make) was dissolved in the mixed solvent which consists of the methyl-ethyl-ketone 75 weight section and the toluene 300 weight section as adhesive resin, the flame retarder and the fire-resistant assistant were added in the solution, mixed stirring was carried out, and fire-resistant solution-like adhesives were prepared.
[0035] (Production of a fire-resistant adhesive film) Fire-resistant solution-like adhesives were applied to polyester film (Unitika, Ltd. make) with a thickness of 25 micrometers by the bar coating machine, were thrown into the drying furnace, a methyl ethyl ketone and toluene were volatilized, and the fire-resistant glue line (40-micrometer thickness) was formed. This obtained the fire-resistant adhesive film.
[0036] Two things which cut the obtained fire-resistant adhesive film to predetermined die length are prepared. (Production of a flat cable) A conductor (what carried out tinning of the rectangular copper wire) is installed in parallel side by side. two or more straight angles whose wire thickness is 50 micrometers at one fire-resistant adhesive film -- After laying another fire-resistant adhesive film on it, lamination and a flat cable were produced for both films by passing between the rolls of two heated at 150 degrees C.
[0037] (Assessment) About the fire-resistant adhesives of examples 1-7 and the examples 1-3 of a comparison, assessment about "electric resistance", "fire retardancy", "combustion gas", and an "adhesive property" was performed so that it might explain below. The obtained result is shown in a table 1 and a table 2.
[0038] (Electric resistance) the conductor (100mm of merits [Conductor]) with which a flat cable adjoins each other -- the electric resistance (applied voltage of 0.5kV) of a between was measured. The case where electric resistance exceeded 1011 ohms was evaluated as "O", the case where electric resistance was 1010ohms or more less than 1011ohms was estimated as "**", and the case where electric resistance was less than 1010ohms was estimated as "x."
[0039] To apply to components for automobiles, a medical-application device, etc. by which high safety is asked for a flat cable here, the electric resistance of 1010ohms or more is required.
[0040] (Fire retardancy and combustion gas) The fire-resistant trial was performed by the approach based on UL-SUB758-VW1. The case where fire retardancy equivalent to a halogen series flame retardant (example 3 of a comparison) was shown here was evaluated as "O", and the case where fire-resistant level was inferior to the halogen series flame retardant was estimated as "x." Moreover, the gas which occurred in the fire-resistant trial was collected, and gas-chromatograph analysis of the gas was performed. Here, the case where halogen gas was not checked was evaluated as "O", and the case where halogen gas was checked was estimated as "x."
[0041] (Adhesive property) After starting the part which fire-resistant adhesive films have pasted up, and the part which the conductor and the fire-resistant adhesive film have pasted up and leaving it for one week in a 60-degree C thermostat, each adhesive strength was measured by tensilon (cage en tech company make). Here, that by which the adhesive strength which exceeds 0.5 kg/cm between adhesive films and a conductor, and a fire-resistant adhesive film was measured was evaluated as "O", that by which 0.3 or more kg/cm the adhesive strength of less than 0.5 kg/cm was measured was evaluated as "**", and that by which the adhesive strength of less than 0.3 kg/cm was measured estimated it as "x."
[0042]
[A table 1]
An example (Weight section) 1 2 3 4 5 6 7 (adhesive resin) Polyester system resin 100 100 100 100 100 100 100 (flame retarder) Melamine SHIANU rate 80 80 80 80 40 10080 Polyphosphoric acid melamine 10 40 60 80 10 10 - Polyphosphoric acid ammonium - - - - - - 10 Deca BUROMO diphenyloxide - - - - - - - (fire-resistant assistant) A calcium carbonate - - - - 40 - - Aluminum hydroxide - - - - 40 - - Antimony trioxide - - - - - - - (assessment) Fire retardancy O O O O O O O Adhesive property O O ** ** O O O Electric resistance O O O ** O O ** combustion gas O OO O O O O [0043]
[A table 2]

The example of a comparison (weight section) 1 2 3 (Adhesive resin) Polyester system resin 100 100 100 (Flame retarder) A melamine SHIANU rate - 100 - Polyphosphoric acid melamine - - - Polyphosphoric acid ammonium - - 120 Deca BUROMO diphenyloxide 60 - - (Fire-resistant assistant) A calcium carbonate - -- Aluminum hydroxide - - - Antimony trioxide 32 - - (Assessment) Fire retardancy O x O Adhesive property O Ox Electric resistance O O x Combustion gas x O O [0044] (Result) A table 1 shows that the result with the fire-resistant adhesives of the examples 1-6 containing polyester system resin, a polyphosphoric acid melamine (polyphosphoric acid system flame retarder), and a melamine SHIANU rate (non-polyphosphoric acid system nitrogen content organic flame retarder) good about the evaluation criteria of "fire retardancy" and "combustion gas" is obtained. Moreover, the fire-resistant adhesives of the example 7 containing polyester system resin, polyphosphoric acid ammonium (polyphosphoric acid system flame retarder), and a melamine SHIANU rate (non-polyphosphoric acid system nitrogen content organic flame retarder) are also known by that the result good about the evaluation criteria of "fire retardancy" and "combustion gas" is obtained. However, although it is small in assessment of "electric resistance" if an example 1 is compared with an example 7, an example 1 is good and this shows that a polyphosphoric acid melamine is desirable also in a polyphosphoric acid system flame retarder.

[0045] Moreover, when a melamine SHIANU rate is made regularity with 80 weight sections and the amount of a polyphosphoric acid melamine is changed with 10 - 80 weight section, in addition to "fire retardancy" and "combustion gas", it turns out that the fire-resistant adhesives of examples 1-3 are good also about "electric resistance." Especially, in addition to "fire retardancy", "combustion gas", and "electric resistance", the fire-resistant adhesives of examples 1 and 2 are good also about an "adhesive property."

[0046] Next, in addition to "fire retardancy", "combustion gas", and "electric resistance", the fire-resistant adhesives of the example 6 which made the amount of a polyphosphoric acid melamine regularity with 10 weight sections, and made the amount of a melamine SHIANU rate the 100 weight sections, and the fire-resistant adhesives of the example 5 which made the amount of a melamine SHIANU rate 40 weight sections, and added the fire-resistant assistant further are also known by that it is good also about an "adhesive property."

[0047] On the other hand, a table 2 shows that the fire-resistant adhesives of the example 1 of a comparison which used the conventional halogen series flame retardant (deca BUROMO diphenyloxide) cannot solve the problem of "combustion gas." Moreover, in the case of the fire-resistant adhesives of the example 2 of a comparison which used only the melamine SHIANU rate as a flame retarder, it turns out that it is a result inadequate about "fire retardancy." It turns out that it is a result with the fire-resistant adhesives of the example 3 of a comparison which used only polyphosphoric acid ammonium as a flame retarder inadequate about an "adhesive property" and "electric resistance."

[0048]

[Effect of the Invention] According to this invention, the fire-resistant adhesives of the non halogen system which has good electric insulation and a good adhesive property, and has the fire retardancy which is moreover equal to a halogen series flame retardant, and the fire-resistant adhesive film using it are offered.

[Translation done.]